OBSERVATIONS ON THE RARE EARTHS: SOME STUDIES IN ABSORPTION SPECTRA

BY

WILLIAM FREDERICK ULRICH

B.S., Southern Illinois University, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

The absorption spectra of the rare earth ions have been the subject of numerous investigations both for the detection and determination of these elements and for more fundamental studies on the nature of the rare earth ions themselves. With the advent of improved instruments, the positions and intensities of the absorption peaks have been evaluated to a high degree of precision, and several studies have been made on the use of these data for the determination of the various lanthanons in the presence of each other (1) (6). Among the factors which have been shown to affect the observed bands are anion species, *p*H, solvent, concentration, temperature, and "neutral" salts (7). The purpose of this investigation was to study some of these factors with respect to their effect upon the absorption spectra of certain rare earth ions. The rare earth beta-diketone chelates were utilized because they provided a means of studying the influence of a number of different, yet related, chelating groups in a large number of solvents. Analytical data were obtained wherever possible.

Experimental and Discussion

Several procedures were studied for the preparation of the rare earth beta-diketone chelates. Of these, the method utilized by Quill and Stites (4) proved the most satisfactory. This consisted of reacting a chloride solution of the rare earth ion with the beta-diketone in a mixture of water and dioxane at a controlled *p*H value. In general, the reactions required about twelve hours for completion. The crystalline products were dried over anhydrous magnesium perchlorate in a vacuum desiccator, then recrystallized from some organic solvent such as carbon tetrachloride.

The molecular weights of selected chelates were determined

in carbon tetrachloride and benzene solutions by means of cryoscopic measurements. The data acquired in these studies indicated that the materials formed only monomers in solution. This is contrary to the findings of other investigators (1) (3), who found evidence for the presence of dimeric forms. The difference in behavior was attributed to the variations involved in the preparation of the derivatives.

The absorption spectra of solutions of acetylacetone derivatives of praseodymium, neodymium, samarium, dysprosium, holmium, and erbium, dibenzoylmethane derivatives of neodymium and erbium, and thenoyltrifluoroacetone derivatives of neodymium and erbium were studied over the visible region of the spectrum in order to evaluate the effects of the chelating groups and the solvents upon the absorption spectra of the rare earth ions. The absorption spectra measurements were made using a Beckman Quartz Spectrophotometer Model DU and a Cary Recording Spectrophotometer.

It was found that certain absorption bands of all of the rare earth ions, except praseodymium, were intensified over their values in simple aqueous solutions. This was indicated by the differences in the absorption coefficients, as evaluated by the relationship k= log Io/I/cL, where k is the absorption coefficient, Io, the intensity of the incident light, I the intensity of the transmitted light, c the concentration, and L the length of the light path through the solution. Thus, the absorption coefficient of the absorption maximum located near 2800 A for erbium chloride solutions was increased over sevenfold in solutions of the erbium chelates. Certain absorption bands of other rare earth ions were affected similarly, though to a lesser degree.

The positions and structures of the absorption bands were observed to vary with the changes in chelating groups and solvents. The greatest shifts in the positions of the absorption bands from their values with aqueous chloride solutions were found with the lighter rare earth ions. The changes in structures of the absorption bands were found to be most

pronounced with the neodymium and erbium ions, although the absorption spectra of other ions were affected. The significance of these changes are discussed.

Measurements on the absorption spectra of solutions of acetylacetone, dibenzoylmethane, thenoyltrifluoroacetone, and some of their rare earth chelates were made in order to study the effect of the rare earth ions upon the reagents. Only minor variations could be detected in the structures, intensities, and positions of the absorption bands.

The solvents effected some changes in the absorption spectra of the rare earth beta-diketone solutions, but no direct relationship could be established between these changes and the dielectric constants of the solvents. Radoitchitch (5) reported similar results with extensive studies on the acetylacetonate derivatives of neodymium and samarium.

The infra-red absorption spectra of a number of the rare earth beta-diketone chelates were measured by means of a Perkin-Elmer Model 21 Double Beam Spectrophotometer. The observed data indicated that the stabilities of these chelates are very similar.

The adherence to Beer's Law shown by many of the chelate solutions indicated that they could be used for quantitative determinations of the rare earth ions. Only the derivatives of praseodymium and samarium showed serious deviations from Beer's Law. These variations may have been caused by the absorption of the reagents.

BIBLIOGRAPHY

(1) Biltz, W., Ann. **331**, 334-58 (1904).

(2) Brantley, J. C., Doctoral Dissertation, University of Illinois, 1949.

(3) Freed, S., Weissman, S. I. and Fortress, F. E., J. Am. Chem. Soc., **63**, 1079-85 (1941).

(4) Quill, L. L. and Stites, J. G., Abstracts of the 115th Meeting of the American Chemical Society, March, 1949, p. 6-0.

(5) Radoitchitch, M., Ann. chim., **13**, 5-87 (1940).

(6) Rodden, J. Research Nat'l. Bur. Standards, **26**, 557 (1941).

(7) Wylie, A. W., J. Soc. Chem. Ind. (London), **69**, 143-47 (1950).

VITA

William Frederick Ulrich was born on November 4, 1926 in Pinckneyville, Illinois. He received his elementary education in that city and was graduated from Pinckneyville High School in 1944. While in the Army Air Force, he attended Photography School in Denver, Colorado. After his discharge from service, he enrolled at Southern Illinois University from which he received the Bachelor of Science degree in June, 1949. He entered the Graduate College of the University of Illinois in September of the same year. During the academic years 1949-50 and 1950-51 he held a teaching assistantship in the Department of Chemistry. From June to August of 1950 he was a research assistant on the University of Illinois Rare Earth Research Program, sponsored by the Offiice of Naval Research. During the academic year of 1951-52 he held a research assistantship, which was sponsored by E. I. duPont deNemours and Company. He was employed as a chemist by the Socony-Vacuum Petroleoum Company, Paulsburo, New Jersey, during the summer of 1951. He is a member of Alpha Chi Sigma, Phi Lambda Upsilon, and Sigma Pi Sigma.